

Approved by

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Date _____

Greenhouse Gas Reference Network Group

NOAA Global Monitoring Division

Analysis of Carbon Dioxide in Air

GMD Technical Procedure

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1. Purpose

This document provides the technical procedures for the analysis of carbon dioxide (CO₂) in air by non-dispersive infrared spectroscopy (NDIR). Carbon dioxide amount of substance is expressed as dry air mole fraction, and is traceable to the SI unit, mass.

2. Scope

NOAA/ESRL/GMD provides compressed gas standards to the World Meteorological Organization/Global Atmosphere Watch (WMO/GAW) community. Natural air or modified natural air standards (tertiary standards) are analyzed for CO₂ against a calibrated set of NOAA secondary standards. The carbon dioxide dry air mole fraction is determined by non-dispersive infrared spectroscopy (NDIR), relative to the WMO CO₂ calibration scale. The WMO CO₂ calibration scale is derived from manometrically-prepared primary standards, which are used to calibrate secondary standards on the same analytical system. The procedures described here only pertain to CO₂ analysis for which a certificate of analysis is issued.

3. Informative References

JCGM (2008), International vocabulary of metrology — Basic and general concepts and associated terms (VIM), JCGM 200:2008.

Lee, J.-Y., H.-S. Yoo, K. Marti, D.M. Moon, J.B. Lee, and J.S. Kim (2006), Effect of carbon isotopic variations on measured CO₂ abundances in reference gas mixtures, J. Geophys. Res. 111, D05302, doi: 10.1029/2005JD006551.

Stern, Nicholas H., The Global Deal: Climate Change and the Creation of a New Era of Progress and Prosperity, Public Affairs press, 2009.

Tans, P., Zhao C., Kitzis, D., (2009) WMO GAW Report 194, 15th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques, Jena, Germany, 7-20 September 2009 (WMO TD No. 1553), pp. 101 - 104, April 2011.

Tohjima, Y., K. Katsumata, I. Morino, H. Mukai, T. Machida, I Akama, T. Amari, and U. Tsunogai (2009), Theoretical and experimental evaluation of the isotope effect of NDIR analyzer on atmospheric CO₂ measurement, J. Geophys. Res. 114, D13302, doi: 10.1029/2009JD011734.

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VIM3, 2007 International Vocabulary of Metrology – Basic and General Concepts and Associated Terms, ISO/IEC Guide 99, 2007 (Geneva, ISO).

Zhao, C., P.P. Tans, and K.W. Thoning (1997), A high precision manometric system for absolute calibrations of CO₂ in dry air, J. Geophys. Res. 102, 5885-5894.

Zhao, C., and P.P. Tans (2006), Estimating uncertainty of the WMO Mole Fraction Scale for carbon dioxide in air, J. Geophys. Res. 111, D08S09, doi: 10.1029/2005JD006003.

4. Terms and Definitions

analysis system: Includes the detector (NDIR), hardware, and computer used to analyze CO₂ in compressed gas cylinders (synonymous with measurement system).

gas standard: A cylinder of compressed gas with mole fractions assigned by metrological methods or by comparison to higher-level standards, used to characterize the response of an instrument for calibration or quality control purposes. For the purposes of this TP, primary, secondary, and tertiary standards are gas standards.

mole fraction: The ratio of the number of moles of analyte to the total number of moles. Dry air mole fraction is the ratio of the number of moles of analyte to the total number of moles in dry air. Within the scope of this TP, all samples are analyzed for dry air mole fraction.

NDIR: Non-Dispersive InfraRed spectroscopy.

primary standard: A measurement standard established using a primary reference measurement procedure, or created as an artifact, chosen by convention. For GMD, CO₂ primary standards are aluminum cylinders containing dry air, for which the CO₂ mole fraction has been determined using the manometer.

regulator: A device used to reduce the pressure in a gas cylinder (input) to a lower pressure (output). High-purity and Ultra-high purity regulators are used.

reference gas: Gases used in the reference cell of the NDIR.

reference Material: A material, sufficiently homogeneous and stable with respect to one or more specified properties, which has been established to be fit for its intended use in a measurement process. (JCGM 200:2008, 3.6)

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response curve: A function that relates the instrument response to mole fraction, as determined from measurement standards.

secondary standard: A standard whose value is determined through analysis relative to primary standards, for a quantity of the same kind. These standards are used to calibrate the instrument response. Use of secondary standards for routine calibration prolongs the life of primary standards.

target tank: A tertiary standard used for routine monitoring of system performance. The system should be capable of reproducing the assigned value of the target tank (within expected uncertainties).

tertiary standard: A standard whose value is determined through analysis relative to secondary standards, for a quantity of the same kind.

transfer system: Analytical system used to compare primary standards to lower order standards.

WMO/GAW: World Meteorological Organization, Global Atmosphere Watch.

5. Procedures

5.1 Cylinder Handling and Conditioning

Cylinders are stored upright and generally packaged horizontally for shipment. Cylinders can be stored at a wide range of temperatures and conditions as described by the manufacturer, Luxfer Inc. (2004 Limited Warranty for Cylinders Manufactured in the United States). Standards to be calibrated are stored upright in the same room environment as the transfer system. A regulator proven to be suitable for delivery of air to the instrument is attached to each cylinder and checked for leaks after pressurization from the cylinder. Once a leak-tight seal is achieved, the regulator is flushed three times, and stored for some time with the regulator pressurized for at least 24 hours prior to analysis, to allow for gas equilibration before analysis. When scheduled for calibration, the regulator is connected to the system through one port on a multiport stream selection valve. Swagelok quick-connect fittings are used throughout the analysis system. These have been shown to be fully compatible with the analytical method. Gas is introduced to the NDIR until the CO₂ mole fraction stabilizes (within 0.1 ppm). At this point the standard and delivery system is considered conditioned and ready for analysis.

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5.2 Analysis

The transfer system (Fig. 1) consists of a Licor 6252 NDIR analyzer and computer-controlled components to introduce gas to the sample cell (B) and reference cell (A). The NDIR is temperature controlled at $\sim 35^{\circ}\text{C}$. The setpoint temperature is not critical. The housing was designed to ensure a stable temperature ($\pm 0.1^{\circ}\text{C}$) over timescales of a few hours.

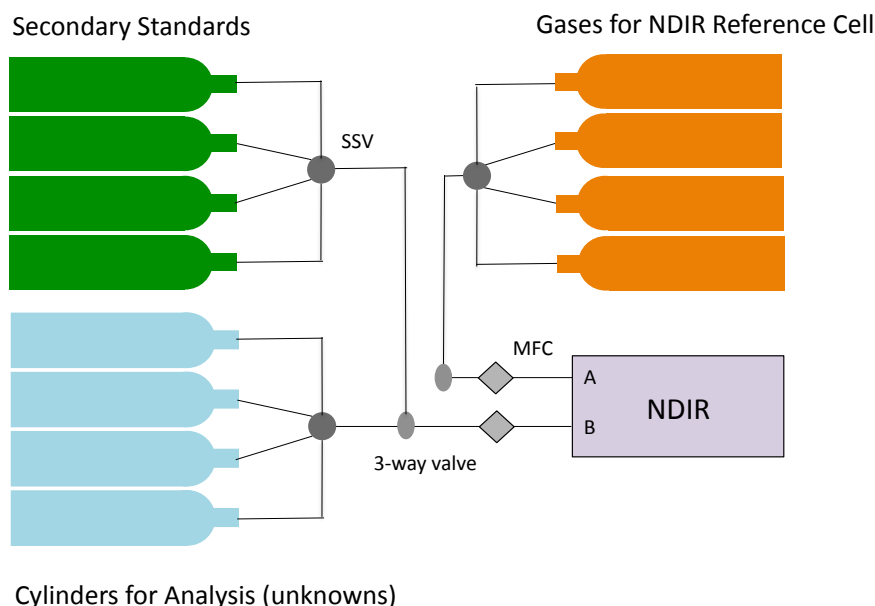


Figure 1: Plumbing schematic for the CO₂ transfer system (SSV: stream selection valve; MFC: mass flow controller). The number of cylinders shown is not meant to be quantitative.

Gas from each cylinder is fed through a conditioned regulator to a multiport stream selection valve via 1/16" O.D. stainless steel tubing. The gas used for the reference varies according to the CO₂ in the unknown. A reference gas is chosen with CO₂ close to, but less than, the lowest CO₂ mole fraction to be encountered in a particular run (sequence). Reference gas flows through a

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two way solenoid valve, then a mass flow controller set to 50 sccm, and finally through reference port “A” of the NDIR. Air from standards to be analyzed (unknowns) and secondary standards (used to define the response curve) is delivered through 16-port stream selection valves to a three-way solenoid valve, which toggles between the multiport valves, and then through a mass flow controller set at 400 sccm leading to sample port “B” of the NDIR.

Each standard to be analyzed (unknown) is compared to a set of four secondary standards spanning the mole fraction range of the unknown. Once flow streams to be used for a particular run are conditioned to their respective gases, a calibration control program is used to alternate between secondary standards and unknowns. For each cylinder, a 90 second flush period is followed by a 30 s data acquisition period. Secondary standards are introduced in ascending order of CO₂ mole fraction.

5.3 Quality Control

Reference materials (RM) are considered calibrated for CO₂ after three calibration runs, where each of the individual calibration results is within 0.03 ppm of the average of the three runs. If one of the calibration results does not agree with the average of the 3 calibration runs to the satisfaction of the analyst or a particular measured standard deviation is greater than 0.03 ppm, the RM is measured a 4th time. A fourth run is usually sufficient to obtain a consistent result. Calibration runs are completed on different days to ensure reproducibility of measurement. The CO₂ reported is determined from the average of all valid analysis runs. It is up to the analyst to flag runs that exhibit characteristics of poor performance. Repeatability of individual calibration runs on different days is typically 0.02 ppm (1 s.d.).

It is critical that assignments made using the analytical system are reproducible. For a sample mole fraction that does not change with time, the system must be capable of reproducing the assigned value (within uncertainties) over the long term. To ensure that the secondary standards are tied to the primary standards, secondary standards are compared to primary standards once each year using the transfer system. Mole fractions of the secondaries are averaged over time or are corrected for drift if measureable drift is confirmed. System stability is verified using a set of surveillance standards (target tanks). These are measured approximately every year to verify that the system is capable of producing reproducible results. Existing standards with well-known CO₂ mole fractions can also be used for this purpose.

6.0 Calculations

The NDIR response for two cycles consisting of four secondaries (Ss1-4) and four unknowns (Ws1-4) is shown in Fig. 2. Each alternate cycle is in opposite order. There are 8 cycles in all

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with the first cycle used only for conditioning and cycles 2 through 8 for the calibration measurement.

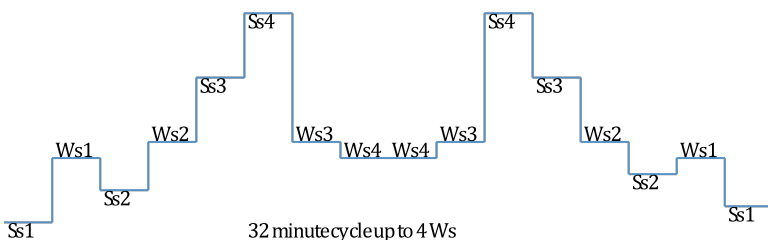


Figure 2: Sample trace of NDIR response for two calibration cycles (S: secondary; W: unknown).

6.1 Mole Fraction

For each cycle, a quadratic fit is determined by generalized least squares using the mole fractions assigned to the secondaries. The CO₂ mole fraction of each unknown is calculated using this quadratic curve fit. The average mole fraction and standard deviation are determined from the 7 cycles.

6.2 Uncertainties

The standard deviations for each 7-cycle calibration run and the standard deviation of the 3 or 4 run average are recorded. The reproducibility associated with the calibration of an unknown is estimated to be 0.06 ppm (95%ile) (see 10.2). The standards uncertainty associated with scale transfer (derived from reproducibility) is combined with the standard uncertainty associated with the primary standards. The resulting expanded uncertainty of the WMO X2007 CO₂ scale, including the uncertainties of the primary standards, is ~0.20 ppm ($k=2$) (see technical procedure TP_primary_manometer.pdf).

7.0 Data Collection and Storage

Raw voltage output from the NDIR is stored to a local computer. After each run, voltage data and calibration metadata are copied to a computer server, which is backed up to a separate server. Bi-monthly, all files are backed up and stored offsite for ~50 weeks.

A GMD database is used to store the following metadata and raw measurement data:

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Filename

Date, instrument, run program.

Port assignments and cylinder serial numbers for unknown and secondary standards.

Cylinder fill code identifier.

Regulator Identifier

Cylinder pressure.

NDIR output voltage

In addition, GMD updates and maintains a relational database for post-processed calibration data indexed by cylinder serial number. This database contains metadata associated with cylinder filling: Fill date, fill code, gas mixture type, pump used, fill location, end user contact and institution, calibration results and metadata, average mole fraction.

8.0 Safety

It is GMD policy to follow safe working practices when handling compressed gas cylinders and laboratory chemicals. Pressurized cylinders should be secured (except when they are being weighed). Personal protective equipment (PPE) should be used when working with hazardous chemicals or in a high noise environment.

9.0 Documentation

Worksheets are created before each calibration and include the metadata and raw data filename, reference flow rate, standard flows rates for each port to be used, cold bath temperature, and room temperature.

10.0 Appendix

10.1 Equipment

The following equipment are critical for the functions described in this TP.

Item	Manufacturer	Model Number
NDIR	Licor	LI6252 or LI66251
Stream selection Valve	Valco	SC-16

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10.2 Reproducibility

Reproducibility is estimated from repeated analysis of tertiary standards that have been analyzed at least 10 times over a span of at least 10 years and corrected for any apparent drift. The reproducibility of CO₂ assignment is estimated at 0.06 ppm (95%ile) for CO₂ in the range 250-520 ppm (Figure A1).

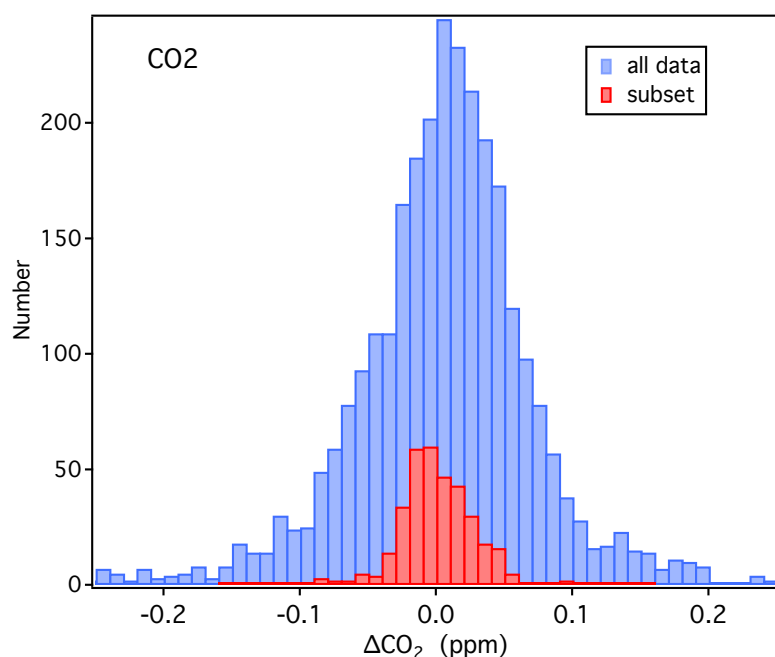


Figure A1: Histogram plot of differences between initial and subsequent CO₂ measurements occurring more than one year apart (blue). Data were restricted to analyses from 2005-2013, pressures > 300 psig. In red, are similar data from a subset of cylinders that have been analyzed more than 10 times and corrected for apparent drift.

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